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643.503



Date of Application and filing Complete Specification: Nov. 3, 1947.

No. 29312/47.

Complete Specification Published: Sept. 20, 1950.

Index at acceptance:—Class 2(iii), C3a5(b: c), C3a13a(2: 3).

COMPLETE SPECIFICATION

A Process for the Production of Oxygen-containing Hydrocarbon Derivatives

I, JAMES GEORGE FIFE, M.Sc., Ph.D., F.R.I.C., Consulting Chemist and Chartered Patent Agent, of Bank Chambers, 329, High Holborn, London, W.C.1, a British subject, do hereby declare the nature of this invention and in what manner the same is to be performed (as communicated to me by N.V. De Bataafsche Petroleum Maatschappij, a Body Corporate organised under the laws of The Netherlands, of 30, Carel van Bylandtlaan, The Hague, Holland), to be particularly described and ascertained in and by the following statement:—

This invention relates to a process for the production of oxygen-containing hydrocarbon derivatives, and more particularly of aldehydes and alcohols.

It is known to produce such derivatives by treating alkenes with carbon monoxide and hydrogen under pressure, as a result of which so-called oxo compounds are formed, which chiefly consist of aldehydes. These can be converted into alcohols in a second stage by hydrogenation.

Hitherto these different stages were carried out separately in different reaction furnaces. Owing to this the process was rather dependent upon circumstances, and a complete apparatus for the production of the alcohols, with the various high pressure furnaces, high pressure separators, high pressure feed pumps, and gas circulation pumps had to be rather extensive.

Furthermore the hydrogenation gas used in the reduction of aldehydes to alcohols had to be substantially free from carbon monoxide, which has an unfavourable influence on the hydrogenation reaction, in particular if a cobalt catalyst is used. The carbon monoxide can be removed by conversion into methane.

By further research concerning the

nature of the reactions occurring and the reaction conditions to be maintained it was found according to this invention that under certain circumstances it is possible to obtain simplifications of the known process, which are attended with a reduction of the apparatus required and consequently with a reduction of the production costs as well as of the investment costs.

Simplifications may be brought about in particular, if gases which are rich in carbon monoxide or completely or substantially completely consist of it, and hydrogen, or gases rich in hydrogen, which can be used in the hydrogenation stage, are separately available.

It was found that the production of oxygen-containing hydrocarbon derivatives by the conversion of alkenes in the presence of an oxo-synthesis catalyst with carbon monoxide and hydrogen under pressure, in which in a first stage oxo compounds are formed which consist chiefly of aldehydes, and are converted into alcohols in a further stage by hydrogenation, may be advantageously carried out by passing the gas remaining after the hydrogenation stage, to an earlier stage.

The process may be carried out by mixing the hydrogen, or hydrogen-containing gas, remaining after the hydrogenation with the excess of the gas containing carbon monoxide and hydrogen, which originates from the first stage, and by using the mixture, if necessary, after it has been adjusted to the correct composition by the addition of a gas which is rich in carbon monoxide, again for the oxo reaction.

An important advantage of the invention consists in that no separate cycle with circulation pump need be used for the hydrogen, since the latter is used for the oxo reaction, if necessary, after addition

of a gas which is rich in carbon monoxide.

Another advantage of the process according to the invention is that the two reactions can now be carried out in a single high pressure vessel as a result of which the investment costs for the apparatus can be considerably reduced.

Another advantage is that no removal of carbon monoxide from cycle gas, if used in the hydrogenation stage, is required. The advantages can be obtained separately or in combination dependent on the particular modification of the process used.

The invention will now be further described by way of example with reference to the accompanying drawings in which:

Fig. 1 shows diagrammatically an apparatus for carrying out the process,

Fig. 2 shows diagrammatically another apparatus for carrying out the process of the invention, and

Fig. 3 illustrates diagrammatically a third apparatus for carrying out the process of the invention.

Referring to Fig. 1 of the drawings a cylindrical inner vessel 2 is disposed in the high pressure vessel 1. The inner vessel contains a cooling or heating device 3, while in the annular space round vessel 2 a cooling or heating device 4 is fitted. Gases leaving the high pressure vessel through conduit 8, are passed through a heat exchanger 5, in which the products to be converted, which are introduced together with suspended oxo-synthesis catalyst through conduit 9, are pre-heated, and returned to the reaction space in the inner vessel 2 with the aid of a circulation pump 6, after a gas rich in carbon monoxide has first been supplied to the cycle gas through conduit 10, so as to obtain the gas composition suitable for the oxo-reaction. In the inner vessel 2 the initial products, which consist of alkenes or of a hydrocarbon fraction rich in alkenes, are contacted with a gas containing carbon monoxide and hydrogen in the presence of a cobalt-containing catalyst, as a result of which aldehydes are chiefly formed under suitable conditions of temperature and pressure. These aldehydes, together with catalyst, flow over the top of vessel 2 into the surrounding circular space, in which the aldehydes are hydrogenated to alcohols with the aid of gas rich in hydrogen, which is supplied through conduit 11. In the upper part of this reaction space dissolved or combined carbon monoxide in the reaction mixture is removed under the influence of this gas rich in hydrogen, while in the lower part the reduction to alcohols chiefly takes place. The level of the liquid in this

reaction space is checked by means of the device 7, which communicates with the valve in the discharge conduit 13 for the products formed.

Excess of gas from the hydrogenation stage is drawn off from the top of the high pressure vessel 1, together with excess of gas from the oxo stage, through conduit 8.

The devices 3 and 4, which serve to cool or heat, are each taken up in a system, with separators 14 and 15 for the separation of vapour formed, e.g. steam.

Referring to Fig. 2 of the drawings, this shows a somewhat different apparatus. The high pressure vessel 1 and the inner vessel 2 correspond to the corresponding vessels in Fig. 1. However, a second inner vessel 16 is provided, which is fixed to the top of the high pressure vessel 1 in such a manner that gases may pass through this wall, e.g. through openings 17. The supply conduit 9 for products to be converted has been lengthened in vessel 1 to approximately the level of the inner vessel 2. The products can now be introduced into the inner vessel 16 in a downward direction and subsequently flow up through the annular space between the inner vessels 2 and 16, upon which the products to be hydrogenated flow down over the top of the inner vessel 2.

In Figs. 1 and 2 of the drawings the inner vessel is intended for the oxo reaction and the outer vessel for the hydrogenation of aldehydes. The spaces may also be used inversely, so that in the outer space the oxo reaction is carried out and in the inner space the hydrogenation. The high pressure vessel 1 may also be divided into two separate reaction spaces in a different manner. They may for example be disposed one above the other, so that for example, in the upper reaction space alkenes are converted into aldehydes, which flow to the lower reaction space, in which the reduction to alcohols takes place. The excess of gas from the hydrogenation stage is then passed through a conduit to the gases from the oxo stage which are conducted in a cycle.

It is also possible to carry out the oxo stage and the hydrogenation stage in separate high pressure vessels, the gases from the hydrogenation stage being conducted, according to the invention towards the gases coming from the oxo stage.

In the process according to the invention the oxo stage and the hydrogenation stage are preferably carried out at the same pressure, which generally lies between 100 and 300 atmospheres.

The temperatures in the two stages as a rule differ slightly. In the oxo stage they usually vary between 50 and 300° C., preferably between 100 and 200° C., de-

pending upon the nature of the initial material and of the oxo-synthesis catalyst used. With the hydrogenation the temperature is generally a little higher and varies between 100 and 350° C., preferably between 150 and 250° C. Because the reaction spaces for the said reactions are each provided with their own cooling or heating device, different temperatures can be maintained without any difficulty. Thus heat will generally be passed through the wall of the inner vessel 2, which does not produce any difficulties, but if necessary the inner vessel 2 may be provided with a heat insulating wall.

The throughout rates in both stages are from 0.5 to 5 litres, preferably 1 to 3 litres of alkenes per litre of reaction space per hour. They may be equal or different in the two stages, which may, e.g. be controlled by a suitable choice of the size of the reaction space.

The quantities of gas in the two stages may vary widely, but will usually be between 50 and 300 litres preferably between 100 and 200 litres (N.T.P.) per sq. cm. of section per hour. The cycle conduit for the gas for the oxo stage is provided with a blow-off conduit not shown in the drawings, in order to be able to control any accumulation of inert gas constituents.

In the hydrogenated final product hydrogen is dissolved, which is liberated when the pressure is reduced. If desired, this hydrogen may be returned to the reaction.

In the process illustrated in Fig. 2 of the drawings hydrogen may be introduced at the bottom of the annular space between the inner vessels 2 and 16, so as to decompose any cobalt carbonyl or hydrocarbonyl formed and displace dissolved carbon monoxide.

The gases for the oxo stage preferably consist of a mixture containing carbon monoxide and hydrogen in a ratio corresponding to the consumption ratio of the reaction which amounts to 1:1 for the pure reaction, but generally is between 1:1 and 1:2 as a result of the accompanying hydrogenation of the aldehydes primarily formed. For the hydrogenation a carbon monoxide free hydrogen-containing gas is desirable.

As oxo-synthesis catalysts there may be used, for example, the well-known catalysts for the synthesis of hydrocarbons from carbon monoxide and hydrogen more particularly cobalt-containing catalysts on a suitable carrier, such as kieselguhr, or other catalysts known for the oxo reaction.

The catalyst is suspended in the initial material and the final product is freed from it in a suitable manner, e.g. with the

aid of filter presses, whereafter the catalyst can be used again.

Referring now to Fig. 3 of the drawings, this shows a further modification according to which three separate stages are used. The advantage of this modification consists in avoiding the removal of carbon monoxide from the cycle-gas used in the hydrogenation stage.

In the apparatus of Fig. 3 of the drawings, the olefin feed enters via line 1 and pump 2. The olefin feed after preheating in heat exchanger 3 is passed to reactor 4 via lines 5 and 6. The catalyst, for example cobalt promoted by a minor proportion of thorium oxide and supported upon diatomaceous earth, is supplied to reactor 4 via pump 7 and lines 6 as a slurry. Carbon monoxide is forced into the system by compressor 8 via lines 9 and 10. This gas is not necessarily pure carbon monoxide, but may contain hydrogen as well as other diluents. However, the carbon monoxide predominates and is in excess with respect to hydrogen. This gas after preheating in heat exchanger 11 is split into two portions; one portion is passed via line 12 to line 6 and then to reactor 4 and the other portion is passed by line 13 to reactor 14. Recycle gas from the first stage is recycled via lines 15 and 16, compressor 17, line 10, heat exchanger 11 and lines 12, 6 and 13.

The temperature in reactor 4 may vary between 80° C. and 200° C. and is preferably 150° C. The pressure may vary between 50 atmospheres and 240 atmospheres, and is preferably 200 atmospheres. Under these conditions the synthesis takes place largely in the liquid phase. The total amount of gas supplied is sufficient to maintain the catalyst in suspension in the liquid reaction mixture and the excess above the reaction requirements is recycled. The residence time of the reaction mixture in reactor 4 may be for example about 10 minutes. The total reaction mixture is preferably, but not necessarily, transferred to a second reactor operated at a slightly higher temperature to effect further reaction. Thus, the reaction mixture is passed via lines 18 and 13 to reactor 14. The temperature in reactor 14 may be, for example, 10° C. to 50° C. higher than in reactor 4. The residence time in the reactor may be, for example, 10 minutes. Additional gas is passed to reactor 14 in an amount sufficient to maintain the catalyst in suspension in the liquid reaction mixture. Reactors 4 and 14 may be made integral, if desired. The total reaction mixture from reactor 14 is cooled and passed via line 19 to separator 20. The gas is recycled via line 15 as before stated. In

order to prevent excessive dilution of the recycled gas, a portion of it may be vented via line 21. As stated above, the gas feed to the first stage consists predominantly of carbon monoxide. The recycle gas recycled via line 16, on the other hand, contains hydrogen and carbon monoxide in a molecular ratio of at least 1:1. However, hydrogen and carbon monoxide are used up in the synthesis in this stage in a ratio somewhat greater than 1:1. The deficiency in hydrogen is supplied by the addition to the recycle gas of a portion of the hydrogen-rich recycle gas from the second stage via valved line 22.

The reaction product of the first stage is passed via pump 23 and line 24 to reactor 25 of the second stage. In the second stage, part of the aldehydes is hydrogenated, and the cobalt-carbonyl (in solution in the reaction mixture) is substantially completely decomposed by the hydrogen-rich recycle gas. This may be effected under a wide variety of conditions. However, merely by way of example the temperature may be 180° C. and the pressure may be 200 atmospheres.

The total reaction mixture is cooled and passed via line 30 to separator 29. The unreacted gas is recycled by compressor 26 via lines 31, 27 and 28. As stated above, a portion of the recycle gas is continuously withdrawn to make up the hydrogen requirements in the first stage. Also, a portion of the hydrogen is consumed in the reaction. The hydrogen requirements for this stage are made up by addition of hydrogen recycle gas from the third stage via valved line 32.

The liquid reaction product from the second stage of the process, now substantially free from carbon monoxide and metal carbonyl, is passed by pump 33 via line 34 to reactor 35 of the third stage. Fresh hydrogen is supplied to this stage through line 36. Recycle gas is supplied by compressor 37 via lines 38 and 39. In the third stage of the process the aldehydes are completely hydrogenated and any trace of metal carbonyl remaining in solution is decomposed. The reaction conditions in the third stage may be the same as or different from those in the second stage and may vary considerably. By way of example, the temperature may be 200° C. and the pressure may be 200 atmospheres. The total reaction product including unused hydrogen is passed overhead via line 40 and cooler 41 to separator 42. The liquid product containing the catalyst in suspension is then passed via line 43 to a low pressure separator 44. The gas from separators 42 and 44 is recycled via line 38 and excess gas is withdrawn to the second stage as described.

The liquid product from separator 44 is passed via line 45 to a separator 46. Here the catalyst settles to a more or less concentrated slurry which is withdrawn from the bottom via line 47 and recycled as described. The liquid product withdrawn from the top of separator 46 still contains some catalyst in suspension. This product is therefore passed via line 48 to a filter 49. The product, free from catalyst, is withdrawn via line 50. Part of the catalyst is usually withdrawn via line 51. However, part or all of it may be passed to mixing tank 52 via line 53 and recycled. Fresh catalyst is added continuously or from time to time to the mixing tank via line 54. Part of the slurry from line 47 may also be passed via line 55 to the mixing tank to make up the slurry.

Specification No. 629,915 claims a process for the preparation of oxygenated compounds in which olefins, carbon monoxide and hydrogen are reacted in the presence of a catalyst comprising iron, cobalt or nickel under conditions to produce oxygenated synthesis products, wherein the reaction products are removed from the synthesis zone, and are purged with hydrogen, after which the hydrogen is removed and the reaction products are passed to a reducing zone, where they are hydrogenated to the corresponding alcohols.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed (as communicated to me from abroad), I declare that what I claim is:—

1. A process for the production of oxygen-containing hydrocarbon derivatives by converting alkenes in the presence of an oxo-synthesis catalyst with carbon monoxide and hydrogen under pressure, in which in a first stage oxo compounds are formed which consist mainly of aldehydes, and are converted into alcohols in a further stage by hydrogenation, characterised in that the hydrogen or hydrogen-containing gas remaining after the hydrogenation is mixed with the excess of the gas containing carbon monoxide and hydrogen, which originates from an earlier stage.

2. A process as claimed in claim 1 in which the hydrogen or hydrogen-containing gas remaining after a later stage, is mixed with the gas, which originates from the first stage, and the mixture, if necessary, after it has been adjusted to the correct composition by the addition of a gas which is rich in carbon monoxide, is used again for the oxo reaction.

3. A process as claimed in claim 1 or

2, wherein the oxo stage is carried out in co-current flow.

4. A process as claimed in claim 1 or 2, wherein the oxo stage is carried out in counter-current flow, liquid initial material flowing from the top to the bottom.

5. A process as claimed in any one of the preceding claims 1, 2 and 4, wherein after the oxo stage the products formed are passed in an upward direction, while passing through hydrogen for removing dissolved and combined carbon monoxide, whereafter the liquid products, flowing downward, are again contacted with a hydrogen-containing gas and hydrogenated therewith.

6. A process as claimed in any one of the preceding claims, which comprises effecting the synthesis in a plurality of stages in separate reaction zones in series, adding hydrogen substantially free from carbon monoxide to the last synthesis stage and recycling the same there-through, recycling hydrogen containing a minor proportion of carbon monoxide in an intermediate stage, adding carbon

monoxide to the first synthesis stage and recycling a carbon monoxide-hydrogen mixture therethrough, withdrawing a portion of recycle gas from said last synthesis stage and adding it to the recycle gas in said intermediate stage, and withdrawing a portion of recycle gas from said intermediate stage and adding it to the recycle gas in said first synthesis stage, the amount of gas transferred being adjusted to maintain the ratio of hydrogen to carbon monoxide in the recycle gas in said first synthesis stage at least equal to 1:1.

7. Oxygen-containing hydrocarbon derivatives when produced by the process claimed in any one of the preceding claims.

Dated the 3rd day of November, 1947.
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Agents for the Applicant.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1950.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies, price 2s. 0d. each (inland) 2s. 1d. (abroad) may be obtained.

643,503 COMPLETE SPECIFICATION

SHEET 1

[This Drawing is a reproduction of the Original on a reduced scale.]

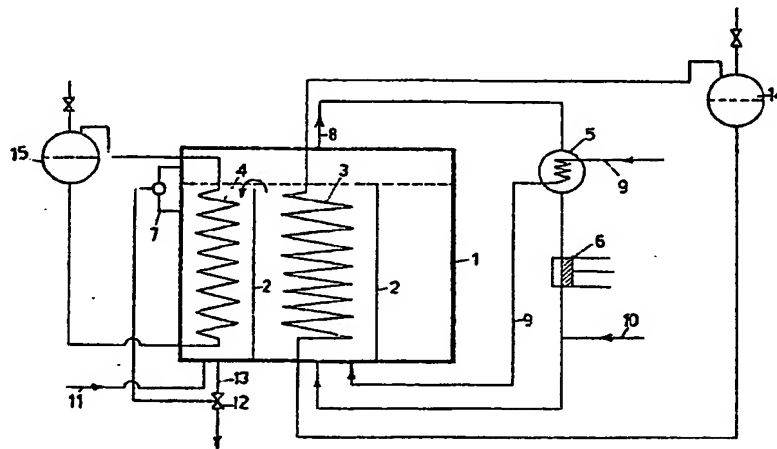


Fig. 1

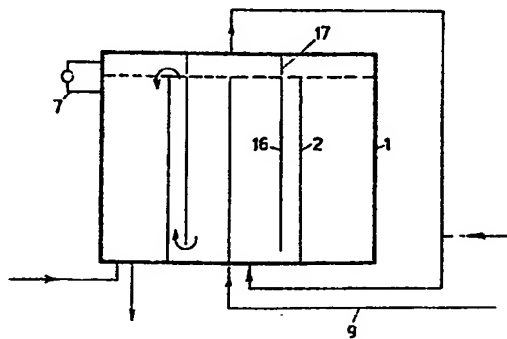
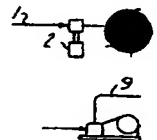


Fig. 2



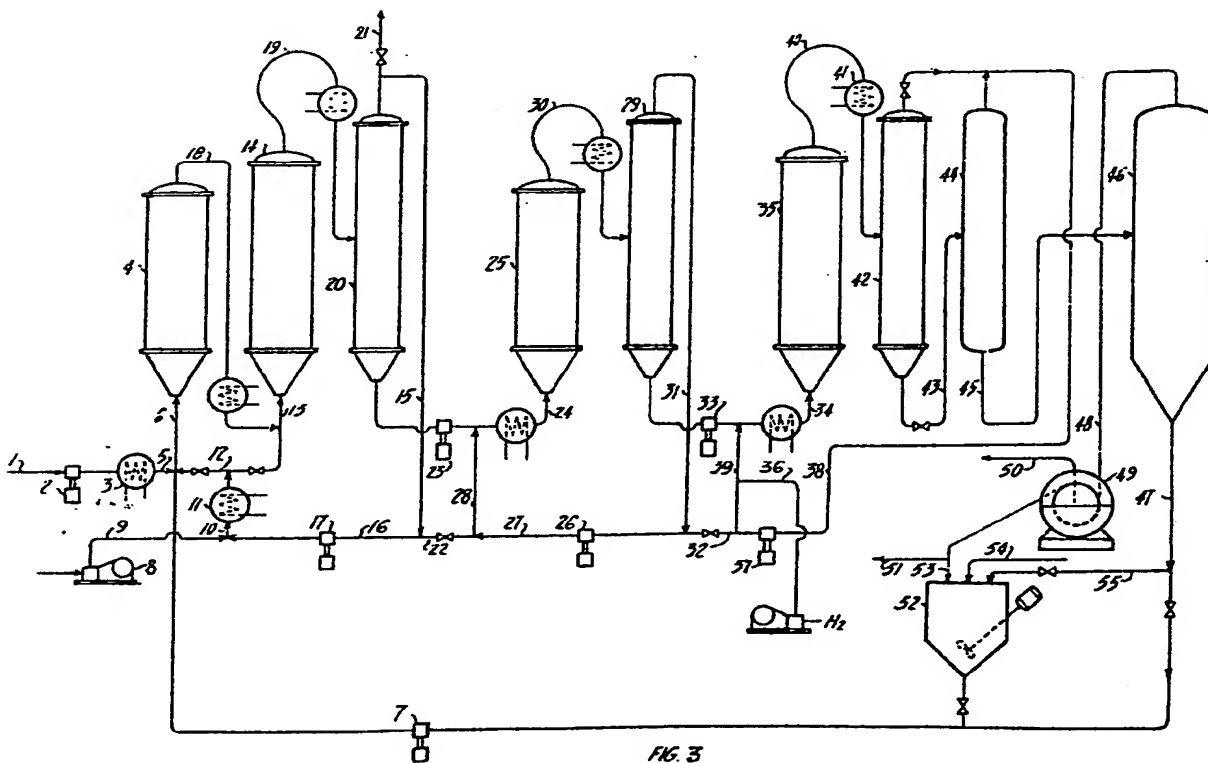
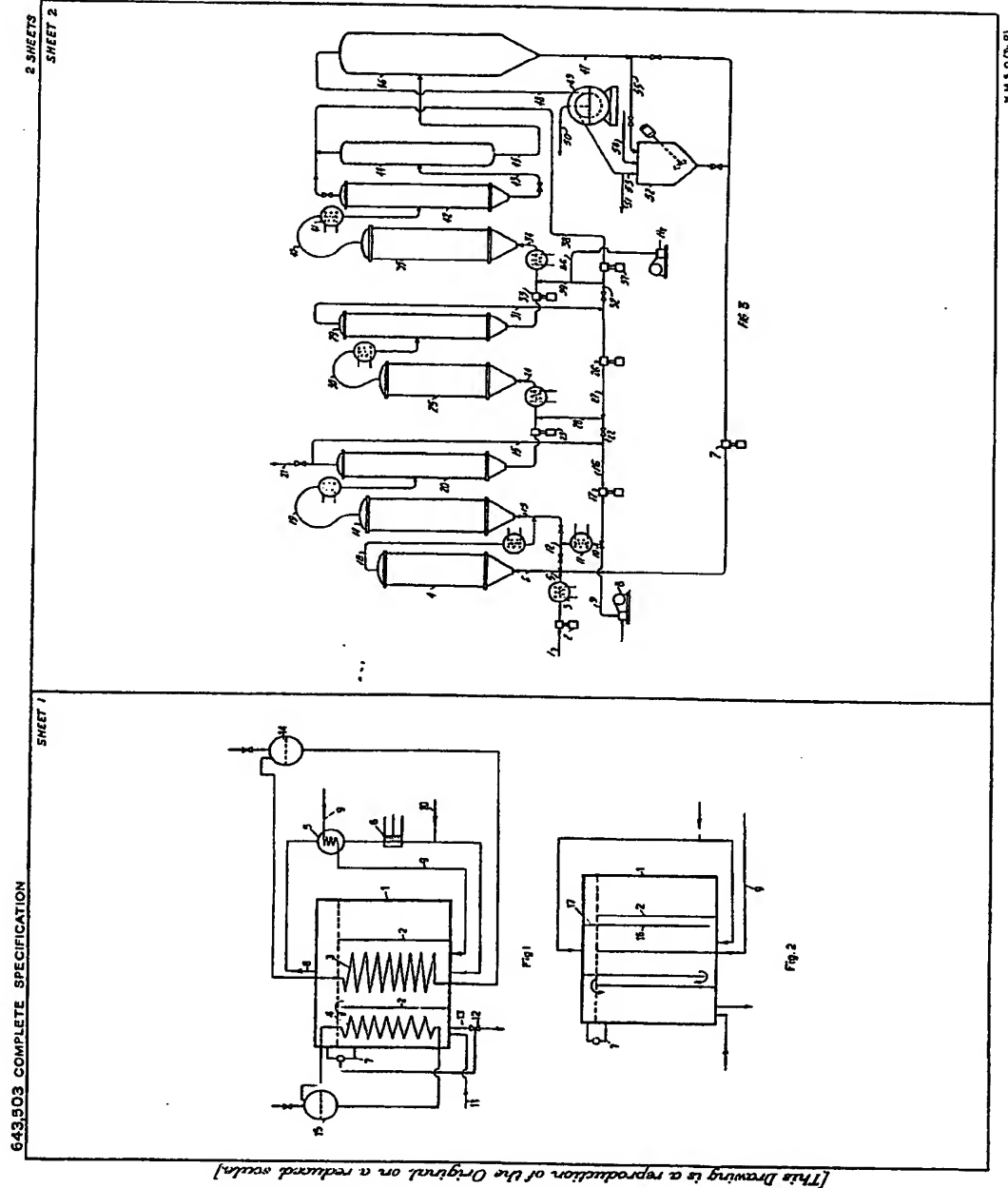


FIG. 3

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M.M.S.O. (7/5)